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Electron Exchange between Bis(η^6 -Arene) Chromium(I)
and Bis(η^6 -Arene) Chromium(0). Comparisons between
Experimental and Calculated Kinetics Parameters.

by

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Comparisons have been made between kinetics parameters for the self exchange of (η^6 -arene) $_2$ Cr(I)/(η^6 -arene) $_2$ Cr(0) (where arene = benzene, toluene, methoxybenzene, biphenyl, ethylbenzoate and chlorobenzene) measured by ESR line broadening in dimethylsulfoxide, with the predictions from contemporary electron-transfer theory. The biphenyl system was additionally studied in a number of other solvents. These reactions provide especially tractable systems with which to test theories of outer-sphere electron transfer since the work terms should be essentially zero, and the inner-shell contributions		

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ΔG_{in}^* to the free energy barrier are small and can be estimated from infra-red spectroscopy combined with crystallographic data. The solvent dependence of the rate constants for $(C_6H_5)_2Cr(I)/(O)$ self exchange was found to be in reasonable agreement with the predictions of the dielectric continuum model. Frequency factors were derived from the experimental rate constants coupled with the estimates of ΔG_{in}^* and values of the outer-shell contribution ΔG_{out}^* obtained by using the dielectric continuum model. These were found to be somewhat (ca. 5-20 fold) larger than the corresponding frequency factors derived from the experimental activation enthalpies combined with the dielectric continuum estimates of the activation entropies. These experimental frequency factors are compared with the estimates obtained from the "reactive collision" and the "ion-pair pre-equilibrium" models. The majority of the experimental frequency factors were found to be numerically closer to the predictions of the former model. However, the experimental values were found to decrease substantially with the addition of substituents on the arene ring, indicating the importance of steric effects. It is suggested that the discrepancies between the experimental results and the predictions of the pre-equilibrium model observed for these and other systems may be due to a combination of steric and nonadiabatic effects.

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Introduction

Outer-sphere electron exchange reactions constitute an especially interesting class of chemical reactions in solution in that it is anticipated that quantitative theoretical descriptions of the reaction dynamics can be provided in many cases. Theoretical treatments of varying levels of complexity (and usefulness) have been developed that allow detailed insight into the physical processes involved.¹ Some recent treatments outline a useful framework within which various aspects of the theories may be tested by comparison with experimental data.²⁻⁴

One question that has arisen is the choice of the frequency factor for outer-sphere reactions.^{2,3} Two alternative models have been proposed. The "reactive collision" model considers that electron transfer occurs upon collision between appropriately energetic reactants, leading to the formulation

$$k = \kappa \Gamma_n Z [\exp(-w/RT) \exp(-\Delta G^*/RT)] \quad (1)$$

where k is the observed (second-order) rate constant for electron exchange, κ is the electronic transmission coefficient, Γ_n is a nuclear tunneling factor, Z is the collision frequency, w is the work required to form the collision complex from the separated reactants, and ΔG^* is the free energy of activation for the elementary electron-transfer step.^{2,3} The alternative "pre-equilibrium" model considers that reaction occurs by activation within a previously formed bimolecular assembly.^{2,3} This leads to the expression

$$k = \kappa \Gamma_n K_p^\circ v_p [\exp(-w/RT) \exp(-\Delta G^*/RT)] \quad (2)$$

where K_p° is the equilibrium constant for formation of the "precursor complex" in the absence of work terms (i.e. when $w = 0$), v_p is the frequency factor for activation within the precursor complex, and the other terms have the same

significance as in Eqn. (1). These two formulations therefore differ in the overall preexponential factor in that the "classical" frequency factor A equals the collision frequency Z in Eqn. (1), but is replaced by the composite term $K_p^\circ v_p$ in Eqn. (2). Although the collision formulation is most commonly employed for bimolecular solution reactions including electron transfer processes, the pre-equilibrium model may provide a more appropriate description of outer-sphere electron transfer when the reaction is expected to take place via electron tunneling between weakly interacting species.

Comparisons between the predictions of Eqns. (1) and (2) with experimental data can be made by obtaining estimates of the frequency factor A in two ways. First, the observed rate constant at a given temperature can be combined with theoretical values of ΔG^\ddagger , w , κ , and Γ_n to yield estimates of A [method (a)]. Second, the Arrhenius activation energy, E_a , derived from the observed temperature dependence of k can be corrected for the temperature dependences of κ , Γ_n , and A to yield an "experimental value" of the enthalpic component of ΔG^\ddagger , ΔH^\ddagger . Values of A can then be found by combining this value of ΔH^\ddagger and a value of k at a given temperature with theoretical estimates of ΔS^\ddagger , w , κ , and Γ_n [Method (b)]. Since both methods depend critically upon the assumed values of ΔG^\ddagger or ΔS^\ddagger , w , κ , and Γ_n , it is clearly important to select systems for which these parameters can be estimated with confidence. Suitable redox couples will therefore be those for which the structural differences between the oxidized and the reduced form are known, and preferably small, so that the inner-shell contribution to ΔG^\ddagger can be calculated and Γ_n will be close to unity.⁴ Additionally, it is desirable that the reactants be spherical, or nearly so, and the product of the reactant charges be small, so that the work term, w , is small and the outer-shell (solvent) contribution to ΔG^\ddagger is most likely to conform to the prediction of the conventional dielectric continuum model.

Several tests of Eqns. (1) and (2) have recently been made. Brown and Sutin² studied the self exchange of Ru(III)/(II) couples containing polypyridine and/or ammine ligands in aqueous solution. Better agreement between the experimental rate constants and activation parameters was obtained by using the reactive collision rather than the preequilibrium formulation. Similar findings were reported by Meyer et al in a study of electron exchange of $[\text{Ru}_3\text{O}(\text{CH}_3\text{CO}_2)_6(\text{py})_3]^{+/\circ}$ in dichloromethane.⁵ Systems of this latter type, where one form of the redox couple is uncharged, have the important advantage that the electrostatic work required to form the encounter complex should be essentially zero.

We have recently reported rate constants and activation parameters for the self exchange of various bis(η^6 -arene) $\text{Cr}^{+/\circ}$ couples, $\text{Cr}(\text{C}_6\text{H}_5\text{X})_2^{+/\circ}$, where $\text{X} = -\text{H}, -\text{CH}_3, -\text{OCH}_3, -\text{C}_6\text{H}_5, -\text{COOC}_2\text{H}_5$, or $-\text{Cl}$, in dimethylsulfoxide (DMSO), by using the ESR line-broadening technique.⁶ The self exchange of $\text{Cr}(\text{C}_6\text{H}_5 \cdot \text{C}_6\text{H}_5)_2^{+/\circ}$ was additionally studied in six other solvents. These reactants provide especially suitable systems with which to test models of outer-sphere electron transfer. Besides the likely absence of electrostatic work terms, they have the advantage that the inner-shell components ΔG_{in}^* are small and can be calculated from appropriate structural data. The comparison of rate constants and activation parameters for such a series of redox couples with various ring substituents can therefore provide a means of exploring the influence of reactant asymmetry on the frequency factors for electron exchange. Such comparisons between the experimental rate parameters and the predictions of Eqns. (1) and (2) are given in the present report.

Experimental Section

The synthesis of all bis(η^6 -arene) chromium compounds were described in Ref. 6. Infrared spectra were obtained by means of a Perkin-Elmer 457 spectrometer, by using either KBr pellets or Nujol mulls at room temperature. The reported IR frequencies are accurate to $\pm 0.5 \text{ cm}^{-1}$. The Nujol mulls of the air sensitive Cr(0) complexes were prepared in an argon-filled dry box and the spectra were measured in an argon atmosphere.

Results and Discussion

Reorganization Energies

The contribution to ΔG^* arising from inner-shell reorganization, $\Delta G_{\text{in}}^*(T)$, for each self-exchange reaction was calculated by means of the expression⁷

$$\Delta G_{\text{in}}^*(T) = \frac{2nf_0f_1\Delta a^2k_B T}{(f_0y_1 + f_1y_0)} \quad (3)$$

In Eqn. (3), f_0 and f_1 are the force constants for the metal-arene bonds in the Cr^0 and Cr^{I} oxidation states, Δa is the difference in the corresponding equilibrium bond distances, n is the number of metal-ligand bonds involved and $y_i = hv_i \coth(hv_i/4k_B T)$, where v_i are the observed Cr-arene stretching frequencies for the oxidation state i . [Equation (3) takes into account the nuclear tunneling factor Γ_n at a given temperature; thus $\Delta G_{\text{in}}^*(T)$ is related to the classical inner-shell reorganization energy ΔG_{in}^* by $\Delta G_{\text{in}}^*(T) = \Delta G_{\text{in}}^* - RT \ln \Gamma_n$.⁴ However, Γ_n is close to unity (1.0 - 1.2) for the present systems.] The normal vibrations of $\text{Cr}(\text{C}_6\text{H}_6)_2$ and $\text{Cr}(\text{C}_6\text{H}_6)_2^+$ have been assigned to be of D_{6h} symmetry from the infrared spectra,⁸ so that n can be set equal to two. The force constants f_0 and f_1 in Eqn. (3) refer to the symmetrical stretching vibration of the two arene rings with respect to the chromium atom. The frequencies of these symmetrical vibrations, v_0 and v_1 , have been determined for the $\text{Cr}(\text{C}_6\text{H}_6)_2^{+/0}$ couple to be about 270 cm^{-1} and 279 cm^{-1} , respectively,^{8c} allowing the force constants to be determined

from $f = 5.89 \times 10^{-2} \nu_{\text{y}}$, where m_{y} is the mass of one arene ring. Values of ν_0 and ν_1 for the other arenes studied here are unavailable. However, they are unlikely to be greatly different than for $\text{Cr}(\text{C}_6\text{H}_6)_2^{+/0}$; thus the asymmetrical Y-Cr-Y stretching frequencies ν_0^{a} and ν_1^{a} are within $5\text{--}10 \text{ cm}^{-1}$ for all the Cr(I)- and Cr(0) arenes (Table I). The values of f_0 and f_1 were therefore estimated assuming that $\nu_0 = 270 \text{ cm}^{-1}$ and $\nu_1 = 279 \text{ cm}^{-1}$.

The value of Δa is 0.07 \AA for the $\text{Cr}(\text{C}_6\text{H}_6)_2^{+/0}$ couple as found from X-ray crystallographic data.⁹ For the other Cr(I)/(0) couples, estimates were obtained from the corresponding difference in infrared stretching frequencies by assuming that $\Delta a \propto (f_0^{\text{a}} - f_1^{\text{a}})$, where f_0^{a} and f_1^{a} are the force constants for the asymmetric vibrations obtained from ν_0^{a} and ν_1^{a} using the formula $f^{\text{a}} = 5.89 \times 10^{-2} (\nu^{\text{a}})^2 [m_{\text{Cr}} m_{\text{y}} / (m_{\text{Cr}} + 2m_{\text{y}})]$, where m_{Cr} is the mass of the chromium atom.^{8a,c} The required proportionality constant was determined from the experimental data for $\text{Cr}(\text{C}_6\text{H}_6)_2^{+/0}$. Justification for this procedure is available for metallocenes.¹⁰ The estimates of $\Delta G_{\text{in}}^*(T)$ resulting from inserting the appropriate values of f_0 , f_1 and Δa into Eqn. (3) are given in Table I. It is seen that the values of $\Delta G_{\text{in}}^*(T)$ are mostly below $1\text{--}1.5 \text{ kcal}\cdot\text{mol}^{-1}$, indicating that inner-shell reorganization provides only a small contribution to the electron-transfer barrier. This is expected since the orbital into which the electron is transferred, a_{1g} having d_{z^2} symmetry, is essentially nonbonding¹¹ so that it may contain one or two electrons [as in Cr(I) and Cr(0), respectively] with little change in the metal-arene bonding.

The other contribution to ΔG^* is provided by the "outer-shell" reorganization energy of the surrounding solvent ΔG_{out}^* . This component was calculated by using the dielectric continuum expression¹²

$$\Delta G_{\text{out}}^* = \frac{e^2}{4} \left(\frac{1}{2a_1} + \frac{1}{2a_2} - \frac{1}{r} \right) \left(\frac{1}{D_{\text{op}}} - \frac{1}{D_{\text{s}}} \right) \quad (4)$$

where D_{op} and D_s are the optical and static dielectric constants, respectively, a_1 and a_2 are the radii of the two (spherical) reactants, r is the distance between the two reacting centers in the activated state, and e is the electronic charge. For the reactions considered here, it is reasonable to assume that approximately $r = 2a_1 = 2a_2$ so that Eqn. (4) reduces to

$$\Delta G_{out}^* = \frac{e^2}{4r} \left(\frac{1}{D_{op}} - \frac{1}{D_s} \right) \quad (5)$$

The values of r for each reaction were calculated by assuming that the transition state is formed with the two reactants placed "side-by-side" (i.e. with the arene rings lying in the same plane),⁶ by using the reported bond distances and van der Waals radii.^{9,13} These estimates of r and the resulting values of ΔG_{out}^* obtained from Eqn. (4) by using known values of D_{op} and D_s are given in Table I (see footnotes for data sources). Also listed in Table I are the calculated values of ΔG^* , ΔG_{calc}^* , obtained for each reaction from the sum of the corresponding values of ΔG_{in}^* and ΔG_{out}^* .

In addition to the free energies of reorganization, it is also necessary to calculate values of the enthalpic and entropic components of ΔG^* , ΔH^* and ΔS^* , respectively. The outer-shell component of ΔS^* , ΔS_{out}^* , was determined from the temperature derivative of ΔG_{out}^* :

$$\Delta S_{out}^* = - \left(\frac{d\Delta G_{out}^*}{dT} \right) = \frac{e^2}{4r} \left(\frac{1}{D_{op}^2} \frac{dD_{op}}{dT} - \frac{1}{D_s^2} \frac{dD_s}{dT} \right). \quad (6)$$

The inner-shell component of ΔS^* , ΔS_{in}^* , was calculated from the temperature derivative of ΔG_{in}^* (1) [Eqn. (3)], thereby taking into account the (small) temperature dependence of r_n .⁴ The resulting values of ΔS_{in}^* (-0.3 to -0.6 e.u.) were then summed with the corresponding estimates of ΔS_{out}^* to yield the calculated activation entropies ΔS_{calc}^* listed in Table I.

Comparison of Experimental and Theoretical Kinetics Parameters

As noted in the Introduction, tests of the applicability of Eqns. (1) or (2) to describe the experimental kinetics parameters can be made either by combining the experimental rate constant at a given temperature with a theoretical estimate of ΔG^* [method (a)], or by employing both the rate constant and its temperature derivative along with a theoretical estimate of ΔS^* [method (b)]. The resulting "experimental" frequency factors can be compared with the values of Z and $K_p^0 v_p$ calculated by using various models. Alternatively, the calculated frequency factors can be combined with the observed rate constant and activation parameters to yield "experimental" values of ΔG^* and ΔS^* which can be compared with the corresponding theoretical estimates. Clearly, the reliability with which a given model for calculating frequency factors can be tested depends sensitively on the accuracy with which ΔG^* or ΔS^* can be calculated, and vice versa. However, the experimental enthalpies of activation ΔH^* obtained from the temperature dependence of the rate constants are insensitive to the particular model employed for the frequency factor. Therefore the comparison between the experimental and calculated values of ΔH^* provides a useful independent test of the likely validity of such theoretical reorganization parameters.

Table II contains a comparison of experimental and calculated values of ΔH^* for the various Cr(I)/(0) self-exchange reactions in DMSO. Two "experimental" values of ΔH^* are listed for each reaction. The first type, labelled ΔH_{pe}^* , are equal to the Arrhenius activation energy, $E_a = R \partial \ln k / \partial (1/T)$; these values are consistent with the preequilibrium formulation since the preexponential factor in this model [$\kappa \Gamma_n K_p^0 v_p$, Eqn. (2)] is expected to be essentially independent of temperature. The second type, labelled ΔH_{rc}^* , are uniformly $0.3 \text{ kcal} \cdot \text{mol}^{-1}$ ($= RT/2$) smaller than ΔH_{pe}^* ; these correspond to the use of the reactive collision formulation since the collision frequency Z appearing in Eqn. (1) is expected to be proportional² to $T^{1/2}$. The calculated values of ΔH^* , labelled ΔH_{calc}^* in Table II, were obtained from the corresponding values of ΔG_{calc}^* and ΔS_{calc}^* given in Table I by using

$$\Delta H_{calc}^* = \Delta G_{calc}^* + T \Delta S_{calc}^*.$$

It is seen that both ΔH_{pe}^* and ΔH_{rc}^* are uniformly smaller than the corresponding values of ΔH_{calc}^* by amounts varying from ca. 0.5 - 2 kcal·mol⁻¹. Since the estimates of ΔH_{in}^* are likely to be correct within at least ca. 0.5 kcal·mol⁻¹, it seems likely that these discrepancies are due chiefly to theoretical estimates of the outer-shell component ΔH_{out}^* that are somewhat too large.

Nonetheless, assuming for the moment that the theoretical reorganization parameters ΔG_{calc}^* or ΔS_{calc}^* given in Table I are correct, these quantities can be combined with the experimental rate constants k given in Table II¹⁴ to yield "experimental" estimates of the frequency factors A_a and A_b by using the relations

$$k = A_a \exp(-\Delta G_{calc}^*/RT) \quad (7a)$$

or

$$k = A_b \exp(-\Delta H^*/RT) \exp(\Delta S_{calc}^*/R) \quad (7b)$$

where ΔH^* in Eqn. (7b) is obtained from the experimental Arrhenius slope (most simply by assuming that A_b is independent of temperature, i.e. $\Delta H^* = \Delta H_{pe}^*$). The resulting values of A_a and A_b are listed in Table III, along with the frequency factors A_{calc}^{pe} and A_{calc}^{rc} calculated from the conventional forms of the preequilibrium and reactive collision models given by Eqns. (8) and (9), respectively:^{2,3}

$$\begin{aligned} A_{calc}^{pe} &= \nu_p K^o \exp(-w/RT) \\ &= \left(\frac{\nu_{in}^2 \Delta G_{in}^*}{\Delta G_{calc}^*} \right)^{1/2} \frac{4\pi N r^3}{3000} \exp(-w/RT) \end{aligned} \quad (8)$$

$$\begin{aligned} A_{calc}^{rc} &= Z \exp(-w/RT) \\ &= (N/10^3) [8\pi k_B T (m_1 + m_2) / m_1 m_2]^{1/2} r^2 \cdot \exp(-w/RT) \end{aligned} \quad (9)$$

where N is Avogadro's number, m_1 and m_2 are the masses of the two reactants, w is

the electrostatic work required to form the collision complex from the separated reactants, and $\nu_{in} (s^{-1})$ is the effective frequency of the inner-shell motion (metal-ligand vibration); this was obtained from the symmetrical stretching frequencies ν_0 and ν_1 (270 and 279 cm^{-1} , respectively) using⁴

$$\nu_{in} = C[2\nu_0^2\nu_1^2/(\nu_0^2 + \nu_1^2)]^{1/2},$$

where C is the velocity of light. Since one of the reactants is uncharged, it is assumed that $w = 0$.¹⁴

Inspection of Table III reveals that the "experimental" frequency factors A_a are, in the majority of cases, close to (within a factor of two of) the values of A_{calc}^{rc} , although ca. 5-20 fold smaller than A_{calc}^{pe} . The frequency factors A_b derived from the experimental rate constants and the activation energies along with ΔS_{calc}^* [Eqn. (7b)] are seen to be significantly smaller, ca. 1/20 of the corresponding values of A_a (Table III). These latter discrepancies result from the differences between the experimental and calculated values of ΔH^* (Table II), since the determination of A_a utilizes ΔG_{calc}^* , whereas the determination of A_b employs only the entropic component ΔS_{calc}^* [Eqns. (7a) and (7b)]. On the basis of the present evidence, it is difficult to decide whether A_a or A_b more closely approximates the true frequency factors; clearly the choice depends upon whether ΔG_{calc}^* or ΔS_{calc}^* are considered more reliable. It has been suggested² that the activation entropy ΔS^* can be taken as zero for self-exchange reactions since $\Delta S_{in}^* \approx 0$ and ΔS_{out}^* is also predicted to be approximately zero from the dielectric continuum model. If indeed $\Delta S^* \approx 0$, then the smaller frequency factors A_b will be approximately correct. However, since the experimental activation enthalpies are smaller than the calculated values, it is likely that there would be a corresponding discrepancy between the actual and calculated activation entropies via a "compensation effect",¹⁵ so that $\Delta S^* < \Delta S_{calc}^*$. For example, the effect could arise from an increase in specific solvent polarization required to form the transition-state from the separated reactants, yielding an unexpected negative contribution to both ΔH^* and ΔS^* . Consequently, the actual

frequency factors may well be larger than A_b , and close to A_a . The latter corresponds to the situation in which the discrepancies between the actual and calculated enthalpic and entropic components of ΔG^* cancel, so that the actual free energies of activation approximately equal ΔG^*_{calc} .

The comparison between the predictions of the preequilibrium and collision models and the experimental kinetic parameters can equivalently be presented in terms of reorganization energies. Table IV contains values of free energies of activation ΔG^*_{pe} and ΔG^*_{rc} obtained from the observed rate constants by using frequency factors calculated from the preequilibrium and collisions models, respectively [Eqns. (8) and (9)]. Listed alongside are the theoretical estimates ΔG^*_{calc} from Table I. It is seen that the corresponding values of ΔG^*_{rc} and ΔG^*_{calc} for most of the reactions agree closely (within $0.3 \text{ kcal}\cdot\text{mol}^{-1}$), paralleling agreement between A_a and $A_{\text{calc}}^{\text{rc}}$, whereas the corresponding values of ΔG^*_{pe} are significantly ($1.5\text{--}2 \text{ kcal}\cdot\text{mol}^{-1}$) larger. Similar results have been obtained previously for several other outer-sphere self-exchange reactions.²⁻⁵ Table IV also contains estimates of activation entropies ΔS^*_{pe} and ΔS^*_{rc} by combining the observed rate constants and activation energies along with $A_{\text{calc}}^{\text{pe}}$ and $A_{\text{calc}}^{\text{rc}}$. It is seen that the values of ΔS^*_{rc} are uniformly 3-6 e.u. more negative than ΔS^*_{calc} , which follows since $A_b < A_a$, $A_{\text{calc}}^{\text{rc}}$ (Table III). The values of ΔS^*_{pe} (-9 to -13 e.u.) seem unreasonably negative; a large increase in the extent of solvent ordering in the transition state compared to that for the separated reactants seems unlikely for the present systems. Consequently, it appears that the values of $A_{\text{calc}}^{\text{rc}}$ listed in Table III are too large.

Another method of estimating the frequency factor involves monitoring the rate constant for a given exchange reaction in several solvents. Since we can write

$$k = A \exp[-(\Delta G^*_{\text{in}} + \Delta G^*_{\text{out}})/RT] \quad (10)$$

if ΔG^*_{out} is given by the dielectric continuum model [Eqn. (5)], then

$$\log k = \log A - \Delta G_{in}^*/2.303RT - \frac{e^2}{2.303 \times 4\pi RT} \left(\frac{1}{D_{op}} - \frac{1}{D_s} \right). \quad (11)$$

Therefore, a plot of $\log k$ versus $(1/D_{op} - 1/D_s)$ should allow A to be obtained from the intercept, and r from the slope. Such a plot is shown for the $\text{Cr}(\text{C}_6\text{H}_5 \cdot \text{C}_6\text{H}_5)_2^{+/0}$ self-exchange reaction in seven solvents in Figure 1. The rate data are taken from Ref. 6, and were corrected for the effects of diffusion in the conventional manner by using $k^{-1} = k_{app}^{-1} - k_{diff}^{-1}$, where k_{app} is the measured (apparent) rate constant, and $k_{diff} = 8RT/3000\eta$, where η is the solvent viscosity. (This correction turned out to be small, yet significant in several solvents.) The values of k are also listed in Table V.

It is seen that the variation of k among most of the solvents studied is approximately in accord with Eqn. (1), suggesting that the dielectric continuum model provides a reasonable description of the solvent influence upon ΔG^* . The straight line drawn through the points has a slope of 3.9 and a y-intercept of 10.1. The resulting value of r , 15.5 Å, is roughly comparable to the value, 11.6 Å (Table I), deduced from the reactant structure by assuming a side-by-side configuration in the transition state. Assuming that $\Delta G_{in}^* = 1.3 \text{ kcal} \cdot \text{mol}^{-1}$ (Table I), a frequency factor A of ca. $9 \times 10^{10} \text{ M}^{-1} \text{ sec}^{-1}$ is obtained. Considering the lengthy extrapolation of Fig. 1 necessary to determine A , this value is in reasonable agreement with A_a , A_b and also A_{calc}^{rc} , but again is markedly smaller than A_{calc}^{pe} (Table III).

Table V also contains values of A_a and A_b , determined for the self exchange of $(\text{C}_6\text{H}_5 \cdot \text{C}_6\text{H}_5)_2\text{Cr(I)/(0)}$ in each solvent, which were obtained from the experimental data as in Table III. As expected, the values of A_a are largely independent of the solvent, although the values of A_b do vary somewhat and are 1/3 - 1/15 of those for A_a . This variation of A_b with the solvent most likely arises from a solvent dependence of the outer-shell entropy term ΔS_{out}^* which is larger than calculated by using the dielectric continuum model. However, it is seen from the values of

ΔH_{pe}^* and ΔH_{rc}^* also listed in Table V that the major part of the solvent dependence of k arises from variations in the enthalpic component, as predicted from theory.

Since the collision model yields frequency factors that are in closer agreement with the experimental results than are the frequency factors obtained from the simple preequilibrium model, it might be inferred that the former model provides a more accurate description of the physical events leading to electron transfer; i.e., that outer-sphere electron transfer is consummated by collision between suitably activated reactants rather than by vibronic excitation within a preformed bimolecular assembly. However, such a conclusion may be unwarranted. Both A_{calc}^{pe} and A_{calc}^{rc} were calculated by assuming that the reactions are adiabatic, i.e. that $\kappa = 1$. Some recent calculations^{4,16} indicate that substantially nonadiabatic pathways ($\kappa \sim 10^{-3} - 10^{-2}$) may predominate even for $Fe(OH_2)_6^{3+/2+}$. Values of κ below unity for the present system would tend to bring A_{calc}^{rc} into closer agreement with A_a and A_b . A related point is that a steric factor arising from the nonspherical shape of the reactants should probably be included in the overall frequency factor. This contention is supported by the observation that both A_a and A_b fall significantly as substituents are added to the arene rings, to an extent that is greater for larger substituents (Table III). Thus the values of both A_a and A_b for $Cr(C_6H_5 \cdot C_6H_5)_2^{+/0}$ self exchange are about fourfold less than for $Cr(C_6H_6)_2^{+/0}$, even though the values of A_{calc}^{pe} and A_{calc}^{rc} are slightly greater for the latter reaction. Even the parent arene reactants $Cr(C_6H_6)_2^{+/0}$ are not spherical; reaction may occur preferentially, for example, with the arene rings in a "side-by-side", rather than "vertically stacked" configuration.^{6,17} Such steric selectivity would yield smaller values of A_{calc}^{pe} and A_{calc}^{rc} than obtained by using the conventional formulas [Eqns. (8) and (9)] which refer to spherical structureless reactants.

Further, the expression previously used²⁻⁵ for the precursor "stability constant" $K_p = (4\pi N r^3 / 3000) \exp(-w/RT)$, appearing in Eqn. (8) may yield incorrectly large estimates of K_p and hence $A_{\text{calc}}^{\text{pe}}$. This expression refers to the formation of contact pairs between two spherical species. It seems more appropriate to visualize K_p as describing the probability that one reactant is present in a given inclusion volume surrounding the other reactant within which electron transfer can occur. Most simply, the magnitude of this volume can be determined by

$$K_p = [4\pi N (d_2^3 - d_1^3) / 3000] \exp(-w/RT) \quad (12)$$

where d_1 is the minimum (contact) distance between the reactants, and d_2 is the maximum distance over which electron tunneling can effectively occur. If, for example, $d_2 - d_1 = 1 \text{ \AA}$, Eqn. (1) leads to values of K_p and hence $A_{\text{calc}}^{\text{pe}}$ for the present systems that are factors of 2-3 smaller than using Eqn. (8). However, in reality κ_p will continuously decrease as the internuclear distance increases, rather than exhibit the discontinuity that is presumed in Eqn. (12).¹⁹

Substantially (≥ 10 -fold) smaller values of K_p can also be deduced using this model by taking into account the nonsphericity of the reactants and assuming that only certain precursor structures, such as a "side-by-side" configuration, result in electron transfer.

Consequently the values of $A_{\text{calc}}^{\text{pe}}$ obtained by taking such steric and tunneling factors into account could become comparable to the experimental estimates of A_a and A_b . Also, the apparently good agreement seen between $A_{\text{calc}}^{\text{rc}}$ and A_a and A_b is probably misleading since the inclusion of reasonable steric factors for the present reactants into the collisional model [Eqn. (9)] would almost certainly yield values of $A_{\text{calc}}^{\text{rc}}$ which are markedly too small.

Conclusions

By and large, the experimental kinetics parameters are in reasonable agreement with the predictions from conventional electron-transfer theory, at least if the collision model is used to provide estimates of the effective frequency factors. However, it is interesting to note that the deviations observed between experiment and theory are qualitatively similar to those seen previously for other self-exchange reactions. Thus it has been found that $\Delta H^* < \Delta H^*_{\text{calc}}$ and $\Delta S^* < \Delta S^*_{\text{calc}}$ for ferricinium/ferrocene in a number of solvents,²⁰ and for $\text{Ru}(\text{NH}_3)_4\text{bpy}^{3+/2+}$ in aqueous media.² Most likely, these discrepancies reflect a limitation of the dielectric continuum model, possibly arising from changes in short-range reactant-solvent interactions required to form the encounter complex "solvent cage" prior to electron transfer. The requirement of forming a particular encounter geometry, with the two reactants essentially in contact so to maximize the transmission coefficient, may partly be responsible for the experimental frequency factors being markedly smaller than those calculated than are obtained using a simple model involving activation of a precursor complex formed in a prior equilibrium step. However, the simple collision model appears to have greater practical utility for outer-sphere processes, at least for the purpose of making numerical calculations.

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TABLE I - Calculated Reorganization Energies and Related Parameters for the Self-Exchange of bis(η^6 -Arene)Cr(I)/Cr(0) in DMSO at 22°C.

Arene	C ₆ H ₆	C ₆ H ₅ CH ₃	C ₆ H ₅ OCH ₃	(C ₆ H ₅) ₂	C ₆ H ₅ COOC ₂ H ₅	C ₆ H ₅ Cl
r(Å) ^a	7.3	8.4	7.8	11.6	9.6	8.6
Δa(Å)	0.07	0.06	0.08	0.07	0.04	0.04
v ₁ ^a , v ₀ ^a (cm ⁻¹)	490,466	489,470	490,464	489,465	480,468	481,468
ΔG _{in} [*] (T) (kcal·mol ⁻¹) ^b	1.15	0.85	1.55	1.30	0.45	0.50
ΔG _{out} [*] (kcal·mol ⁻¹) ^c	4.9	4.3	4.6	3.1	3.8	4.2
ΔG _{calc} [*] (kcal·mol ⁻¹) ^d	6.1	5.2	6.2	4.4	4.3	4.7
ΔS _{calc} [*] (cal·deg ⁻¹ ·mol ⁻¹) ^e	-1.0	-0.9	-1.2	-0.9	-0.8	-0.8

^aThe average "side-by-side" internuclear distance (Cr⁰-Cr⁺) as estimated from molecular models.

^bCalculated using Eqn. (3).

^cCalculated using Eqn. (4); Sources for dielectric constants: D_{op}, Reference 22; D_s, Reference 21.

^dThe sum of ΔG_{in}^{*}(T) and ΔG_{out}^{*}.

^eThe sum of ΔS_{in}^{*}(T) and ΔS_{out}^{*}. ΔS_{in}^{*}(T) is taken from the temperature derivative of ΔG_{in}^{*}(T):

$$\Delta S_{in}^*(T) = - \left[\frac{d \Delta G_{in}^*(T)}{dT} \right] = - \frac{h\nu_{in}}{T} \left(1 - \frac{h\nu_{in}}{2kT} \operatorname{csch} \frac{h\nu_{in}}{2kT} \right)$$

where ν_{in} is the average frequency of inner shell motion (symmetric stretch) from $\nu_{in} = [2\nu_0^2\nu_1^2/(\nu_0^2 + \nu_1^2)]^{1/2}$. ΔS_{out}^{*} is calculated from Eqn. (6) using values of dD_{op}/dT and dD_s/dT obtained from sources given in footnote (c).

TABLE II - Comparison of Experimental and Calculated Enthalpies of Activation for the Self-Exchange of bis(η^6 -Arene)Cr(I)/Cr(0) in DMSO at 22°C.

Arene	-----Experimental-----		Calculated	
	^a $10^{-7} \text{ k M}^{-1} \text{ sec}^{-1}$	^b ΔH_{pe}^* $\text{kcal} \cdot \text{mol}^{-1}$	^c ΔH_{rc}^* $\text{kcal} \cdot \text{mol}^{-1}$	^d ΔH_{calc}^* $\text{kcal} \cdot \text{mol}^{-1}$
C_6H_6	6.0	4.0	3.7	5.7
$\text{C}_6\text{H}_5\text{CH}_3$	3.3	4.6	4.3	5.0
$\text{C}_6\text{H}_5\text{OCH}_3$	7.7	3.6	3.3	5.8
$(\text{C}_6\text{H}_5)_2$	23	2.6	2.3	4.2
$\text{C}_6\text{H}_5\text{COOC}_2\text{H}_5$	32	2.3	2.0	4.1
$\text{C}_6\text{H}_5\text{Cl}$	20	2.9	2.6	4.4

^a Experimental rate constant, taken from Reference 6.

^b Obtained from $\Delta H_{pe}^* = E_a$, where E_a is the Arrhenius activation energy.

^c Obtained from $\Delta H_{rc}^* = E_a - 0.5 \text{ RT}$.

^d Calculated enthalpies of activation, obtained from $\Delta H_{calc}^* = \Delta G_{calc}^* + T\Delta S_{calc}^*$ using values of ΔG_{calc}^* and ΔS_{calc}^* given in Table I.

TABLE III - Comparison of Calculated and "Experimental" Frequency Factors
 $(M^{-1}sec^{-1})$ for the Self-Exchange of $bis(\eta^6\text{-Arene})Cr(I)/(0)$
in DMSO at 22°C.

Arene	Calculated Frequency Factors		"Experimental" Frequency Factors	
	A_{calc}^{pe} (Eqn. 8)	A_{calc}^{rc} (Eqn. 9)	A_a (Eqn. 7a)	A_b (Eqn. 7b)
C_6H_6	3.5×10^{12}	2.5×10^{11}	1.7×10^{12}	9.1×10^{10}
$C_6H_5CH_3$	5.3×10^{12}	3.1×10^{11}	2.4×10^{11}	1.3×10^{11}
$C_6H_5OCH_3$	5.9×10^{12}	2.5×10^{11}	2.8×10^{12}	6.5×10^{10}
$(C_6H_5)_2$	1.7×10^{13}	4.7×10^{11}	4.5×10^{11}	3.1×10^{10}
$C_6H_5COOC_2H_5$	9.1×10^{12}	3.3×10^{11}	4.9×10^{11}	2.4×10^{10}
C_6H_5Cl	6.2×10^{12}	3.0×10^{11}	6.1×10^{11}	4.2×10^{10}

TABLE IV - Comparison of "Experimental" and Calculated Free Energies and Entropies of Activation for the Self-Exchange of bis(η^6 -Arene)Cr(I)/(O) in DMSO at 22°C.

Arene	Activation Free Energies, kcal·mol ⁻¹			Activation Entropies, cal·deg ⁻¹ ·mol ⁻¹		
	^a ΔG^*_{pe}	^b ΔG^*_{rc}	^c ΔG^*_{calc}	^d ΔS^*_{pe}	^e ΔS^*_{rc}	^f ΔS^*_{calc}
C ₆ H ₆	6.4	5.0	6.1	-8.1	-4.4	-1.0
C ₆ H ₅ CH ₃	7.0	5.2	5.2	-8.1	-3.1	-0.9
C ₆ H ₅ OCH ₃	6.6	4.7	6.2	-10.1	-4.9	-1.2
(C ₆ H ₅) ₂	6.5	4.4	4.4	-13.2	-7.1	-0.9
C ₆ H ₅ COOC ₂ H ₅	6.0	4.0	4.3	-12.1	-7.0	-0.8
C ₆ H ₅ Cl	6.1	4.3	4.7	-10.6	-5.7	-0.8

^aObtained from $\Delta G^*_{pe} = -RT \ln(k/A^{\text{pe}}_{calc})$

^bObtained from $\Delta G^*_{rc} = -RT \ln(k/A^{\text{rc}}_{calc})$

^cSum of ΔG^*_{out} and $\Delta G^*_{in}(T)$; taken from Table I.

^dObtained from $\Delta S^*_{pe} = (\Delta G^*_{pe} - \Delta H^*_{pe})/T$; ΔH^*_{pe} taken from Table II.

^eObtained from $\Delta S^*_{rc} = (\Delta G^*_{rc} - \Delta H^*_{rc})/T$; ΔH^*_{rc} taken from Table II.

^fSum of ΔS^*_{out} and $\Delta S^*_{in}(T)$; taken from Table I.

TABLE V - Rate Constants, Activation Parameters and Experimental Frequency Factors $A(M^{-1}sec^{-1})$ for the Self-Exchange of $bis(C_6H_5)_2Cr(I)/(O)$ in Various Solvents at 22°C.

Solvent	$10^{-8} k$ $M^{-1} sec^{-1}$	Activation Enthalpies, Activation Entropies, kcal mol^{-1}						"Experimental" Frequency Factors $M^{-1} sec^{-1}$	
		ΔH_{pc}^*	ΔH_{rc}^*	ΔH_{calc}^*	ΔS_{pc}^*	ΔS_{rc}^*	ΔS_{calc}^*	A_a (Eqn. 7a)	A_b (Eqn. 7b)
C_6H_6/CH_3OH [9/1 v/v]	6.4	2.3	2.0		-12.6	-6.4		2.1×10^{11}	---
Benzonitrile	4.1	2.7	2.4	3.8	-11.9	-6.1	-1.4	4.2×10^{11}	7.7×10^{10}
Dimethylsulfoxide	2.5	2.6	2.3	4.2	-13.2	-7.4	-0.9	4.5×10^{11}	3.1×10^{10}
Dimethylformamide	2.2	3.1	2.3	4.1	-11.5	-5.8	-1.9	5.5×10^{11}	1.0×10^{11}
C_6H_6/CH_3OH [1/4 v/v]	1.6	3.7	3.4		-10.2	-4.4		6.8×10^{11}	--
Propylene Carbonate	1.6	3.9	3.6	4.5	-9.5	-3.7	-0.8	5.0×10^{11}	1.7×10^{11}
C_6H_6/CH_3OH [1/7 v/v]	1.2	3.8	3.5		-10.2	-4.7		5.8×10^{11}	

^a Experimental rate constant corrected for diffusion (see text), using viscosity data given in Reference 21.

^b Obtained from experimental activation energy E_a assuming that $\Delta H_{pe}^* = E_a$.

^c Obtained from E_a assuming that $\Delta H_{rc}^* = E_a - 0.5$ RT.

^d Obtained as in Table II, using dielectric constants from sources given in footnote h.

^e Obtained from experimental rate constant and A_{pe}^{rc} (Eqn. (8)) as described in footnotes to Table IV.

^f Obtained from experimental rate constant and A_{calc}^{rc} (Eqn. (9)) as described in footnotes to Table IV.

^g Obtained as in Table IV, using dielectric constants from sources given in footnote h.

^h Dielectric constant data required for calculating ΔG_{calc}^* (Eqn. (7a)) and ΔS_{calc}^* (Eqn. (7b)) obtained from following:

D_{op} and D_s for benzene/methanol mixtures obtained by linear interpolation of values for pure solvents. Values of D_{op} for each solvent obtained from Reference 22, except for propylene carbonate, given in L. Simeral. R.L. Amey, J. Phys. Chem. 74, 1443 (1970). Sources for D_s : benzene, methanol, dimethylsulfoxide - Reference 21. Benzonitrile - A.A. Maryott, E.K. Smith, "Table of Dielectric Constants of Pure Liquids," Natl. Bur. Stand. U.S. Circ. 514 (1951). Dimethyl formamide - S.J. Bass, W.I. Nathan, R.M. Meighan, R.H. Cole, J. Phys. Chem. 63, 590 (1964). Propylene carbonate - R. Payne, I.E. Theodorou, J. Phys. Chem. 76, 2892 (1972).

Caption to Figure 1

Plot of logarithm of rate constant k for self exchange of $\text{Cr}(\text{C}_6\text{H}_5\cdot\text{C}_6\text{H}_5)_2^{+0}$ in various solvents versus $(1/D_{\text{op}} - 1/D_s)$, where D_{op} and D_s are the optical and static dielectric constants for each solvent.

1. $\text{C}_6\text{H}_6/\text{CH}_3\text{OH}$ (9/1 v/v);
2. benzonitrile;
3. dimethylsulfoxide;
4. dimethylformamide;
5. $\text{C}_6\text{H}_6/\text{CH}_3\text{OH}$ (1/4 v/v);
6. propylene carbonate;
7. $\text{C}_6\text{H}_6/\text{CH}_3\text{OH}$ (1/7 v/v).

Values of k given in Table V; sources for D_{op} and D_s given in footnote h to Table V.

